

QUALITATIVE HEADSPACE GCMS ANALYSIS OF LUNAR REGOLITH AND VOLATILE SIMULANT MIXTURES

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Introduction: Future Artemis missions aim to return the volatile-bearing samples collected near lunar polar craters. We, as advanced curation scientists, are responsible for developing techniques and methodologies for preserving the integrity of returned samples and the science value those samples contain. The extent to which that preservation is possible, and the trade-offs preservation requires (e.g. monetary costs, sample volume limitations) all must be considered. Even less-than-pristine volatile-bearing samples will be of tremendous value to the scientific community seeking to unravel the history of lunar surface volatiles and, more broadly, volatiles in the solar system.

A sample collected on the lunar surface will experience at least five distinctive periods during which any changes here referred to as “alteration” will certainly occur at some scale: collection on the lunar surface; transportation back to Earth; long-term storage; curatorial processing; and allocation/distribution. The Planetary Exploration and Astromaterials Research Lab (PEARL) seeks to understand temperature and pressure effects on returned volatile samples by working with high-fidelity volatile-containing regolith simulants, setting the foundation for the future of cold curation. This abstract is focused on gas-surface interactions between LCROSS volatiles and readily available lunar regolith simulants. Experiments involved analyzing differences in headspace gas composition for various combinations of volatile and regolith simulants using gas chromatography/mass spectrometry (GC/MS).

Experimental Procedure: The volatile simulants were chosen based on the molecules detected during the LCROSS mission.¹ Stock solutions of condensed lunar volatile analytes were: methanol, 7 N ammonia in methanol, and 0.4% hydrogen sulfide in water. The regolith simulants used were primarily JSC-1A and NU-LHT-4M. Additional regolith simulant control studies were



Figure 1. Picture of the nested vial set-up.

conducted with <150 μm sieved sand and KBr. A nested vial sample preparation approach separated the liquid stock solutions from the regolith, eliminating potential matrix effects between liquid and solid phases. Fifteen microliter aliquots of liquid volatile simulants were added to a 2 mL liquid GC vial and capped in atmosphere. An 18G needle punctured the 2 mL GC vial immediately before being transferred and sealed in a 20 mL GC vial containing 0-0.3 g of regolith simulant, see Figure 1. Separating the analytes ensures any changes observed in the total headspace gases is a result of gas-surface and/or gas-gas interactions.

Equipment and Method: Initial GC/MS method development for the separation and identification of relevant headspace gases can be found in Amick, et al. 2023.² The only hardware change is a different column: a TG-1701MS 30 m \times 0.25 mm \times 1.00 μm column.

The vials were sampled at 10°C, room temperature ($\sim 25^\circ\text{C}$) and 50°C. Low temperature samples were kept in a chilled autosampler stage for at least 1 hour prior to sampling. High temperature samples were agitated at 50°C for 5 minutes immediately prior to injection onto the column. Headspace chromatograms were collected for each combination of temperature, regolith, and volatile simulant, including controls without one or both types of analytes, in triplicate.

The chromatogram elution window for each analyte or significant atmospheric gas was identified using the peak mass spectrum cross-referenced with

a NIST MS library search. Each analyte peak was integrated after filtering the mass spectrum trace for the parent or most unique mass-to-charge ratio. For example, the mass-to-charge ratio used to identify, filter for, and integrate the carbon dioxide peak was centered around 44 m/z.

Results: Figure 2 shows the integrated peak area for hydrogen sulfide in all combinations of regolith simulants, temperatures, and the addition of ammonia in methanol solution. Multiple repeat experiments with H₂S and regolith simulants have confirmed hydrogen sulfide is removed from the headspace within 1 hour when exposed to JSC-1A, NU-LHT-4M and sand (not pictured).

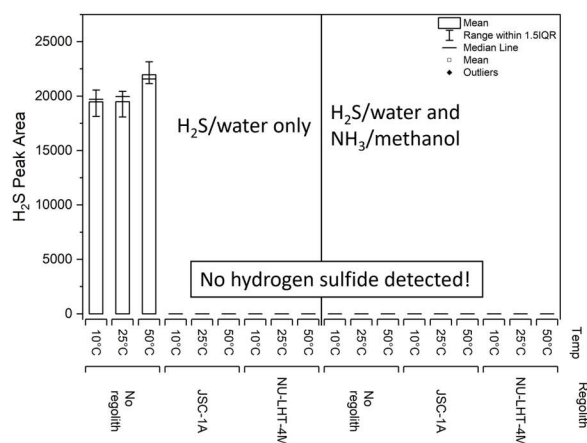


Figure 2. Average hydrogen sulfide peak area detected and identified via GC/MS. The chromatograms were filtered for 33.9-34.1 m/z, centered at the parent MS peak for H₂S, then integrated the peak at the elution time for hydrogen sulfide.

The consumption of H₂S by lunar regolith simulants at different temperatures indicates surface chemistry will be an integral component in sample integrity and preservation. It is important to note that while the effect of surface chemistry on gaseous hydrogen sulfide is intriguing, further investigation into more chemically accurate regolith simulants is necessary and ongoing. The sulfur in hydrogen sulfide is in its most reduced state while off-the-shelf, terrestrially sourced JSC-1A and NU-LHT-4M are more oxidized than most lunar materials,³ which likely leads to different oxidation-reduction reactions than would be expected in lunar regolith.

Figure 3 shows the integrated peak area of carbon dioxide for each sample combination that contained ammonia in methanol solution. The addition of ammonia to the GC vials results in a consistent and reproducible decrease in carbon

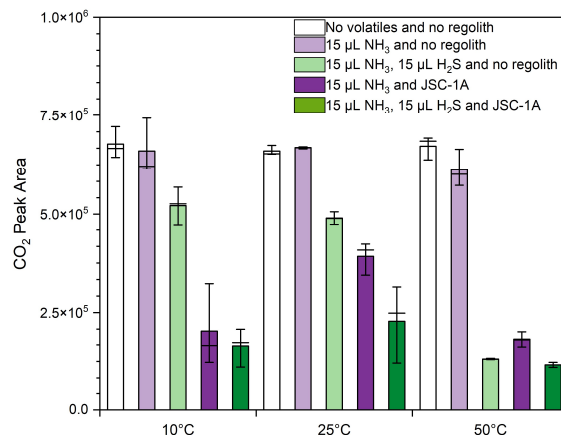


Figure 3. Average CO₂ peak area detected and identified via GC/MS. The chromatograms were filtered for 43.9-44.1 m/z, centered at the parent MS peak for CO₂, then integrated the peak at the elution time for carbon dioxide. JSC-1A was used as the regolith simulant.

dioxide gas, even at 50°C. The effect became more pronounced when JSC-1A or NU-LHT-4M were present. This set of experiments demonstrated that the sample composition will affect the chemical and physical state of each component present. Future spectroscopic and microscopy experiments will be geared towards identifying the cause for the CO₂(g) concentration decrease and the consumption of hydrogen sulfide.

As cold and volatile curation scientists, this information provides necessary insight on how to appropriately handle and analyze volatile bearing returned samples, as well as predict the effect chemical composition has on the various sample phases we will analyze upon return to Earth. Unlike traditional curation of geologic materials, the molecules in a sample cannot be identified or processed using the naked eye or even an optical microscope. Volatile curation will require a combination of analytical techniques, including but not limited to highly sensitive gas and solid/condensed phase spectroscopy. This set of experiments has demonstrated the need for more detailed studies of volatile mixtures with mineralogically and geochemically analogous lunar regolith simulants to prepare for the curation of volatile-rich lunar samples from the south polar region of the Moon.

References: [1] Colaprete, A., et al. (2010) *Science*, 330, (463-468). [2] Amick, C. L., et al.(2023) *Houston, Texas*, [3] Heiken, G. H., et al.(1991) (778-778).